

INORGANIC QUALITATIVE ANALYSIS

Aim : To detect two acidic radicals from different groups and two basic radicals from same group in the given mixture.

PART-I : DETECTION OF TWO ACIDIC RADICALS

On the basis of the reactions with different reagents, the acidic radicals are generally classified into following three groups.

Group	Reagent	Characteristic reaction	Radicals
Group I	Dil. H_2SO_4	Acidic radicals which evolve gases on treatment with dilute Sulphuric acid.	Carbonate (CO_3^{2-}) Sulphite (SO_3^{2-}) Sulphide (S^{2-}) Nitrite (NO_2^-)
Group II	Conc. H_2SO_4	Acidic radicals which evolve gases on treatment with conc. Sulphuric acid.	Chloride (Cl^-) Bromide (Br^-) Iodide (I^-) Nitrate (NO_3^-)
Group III	BaCl_2	Acidic radicals which do not evolve gases with dilute or conc. Sulphuric acid but gives precipitate with Barium chloride solution.	Sulphate (SO_4^{2-})

1. Preparation of Sodium Carbonate Extract :

Mix about 1 g of the given mixture with 2-3 g of pure solid Sodium carbonate in China dish and add about 15 ml distilled water. Boil for 10-15 minutes and filter. The filtrate so obtained is known as Sodium Carbonate extract or Soda extract.

2. Detection of acidic radicals of Group I

Test: Take a pinch of given mixture in a test tube and add 2 ml dilute sulphuric acid and warm. (Do not Boil). Note the observations as given in the table. Confirm the acidic radicals indicated by confirmatory test.

Test	Observation	Inference
Confirmatory test for CO_3^{2-} : (1) Pass the evolved gas through 2 ml clear lime water with the help of bent tube. (2) To the aq. Extract of the given mixture add MgSO_4 .	➤ Brisk effervescence with evolution of colourless and odourless gas. Lime water turns milky White ppt in cold	Carbonate (CO_3^{2-}) Present Carbonate (CO_3^{2-}) confirms
Confirmatory test for SO_3^{2-} : Hold a piece of filter paper dipped in Potassium dichromate solution at the mouth of the test tube.	➤ Colourless gas with the smell of burning sulphur. The paper turns green	Sulphite (SO_3^{2-}) Present Sulphite (SO_3^{2-}) confirms
Confirmatory test for S^{2-} : (1) Hold a piece of filter paper dipped in Lead acetate solution at the mouth of the test tube. (2) To the sodium Carbonate extract, add few drops of Sodium nitroprusside solution.	➤ Colourless gas with the smell of rotten eggs (H_2S gas). The paper turns brownish black Violet colour obtained	Sulphide (S^{2-}) Present Sulphide (S^{2-}) confirms
Confirmatory test for NO_2^- : (1) Hold a piece of filter paper dipped in a mixture of starch and potassium iodide solution at the mouth of the test tube. (2) Mix the given mixture with potassium iodide (KI) add to it conc. sulphuric acid. (3) Acidify Soda extract with acetic acid and add to it conc. Cobalt chloride solution and add solid ammonium Chloride, warm and wait for some time.	➤ Reddish brown coloured pungent smelling gas. The paper turns blue. Evolution of violet fumes Formation of yellow ppt.	Nitrite (NO_2^-) Present Nitrite (NO_2^-) confirms.

3. Detection of acidic radicals of Group II :

Test: Take a pinch of given mixture in a test tube and add one ml conc. sulphuric acid and warm. (Do not Boil). Note the observations as given in the table. Confirm the acidic radicals indicated by confirmatory test.

Test	Observation	Inference
Confirmatory test for Cl⁻ : Silver nitrate Test : Take 2 ml of Sodium Carbonate extract and acidify it with dilute nitric acid.(Nitric acid should be added till no further effervescence is seen). To this add silver nitrate solution.	<div>➤ Colourless pungent odour gas which forms white dense fumes on holding a glass rod dipped in Ammonium hydroxide solution.</div> <div>Formation of white ppt which dissolves in ammonium hydroxide solution.</div>	<div>Chloride (Cl⁻) Present</div> <div>Chloride (Cl⁻) confirms</div>
Confirmatory test for Br⁻ : 1. Perform Silver nitrate test as given above. 2. Layer Test: Take 2 ml Sodium Carbonate extract and acidify it with dilute nitric acid till no further effervescence is seen. To this solution add 1 ml of chloroform or carbon tetrachloride. Then add 1 ml of chlorine water or few drops of conc. nitric acid. Shake the test tube vigourously and allow the layers to separate. Observe the colour of lower layer.	<div>➤ Reddish brown coloured pungent smelling gas.</div> <div>Formation of pale yellow Ppt.which partly soluble in ammonium hydroxide solution.</div> <div>Formation of Brown layer.</div>	<div>Bromide (Br⁻) Present</div> <div>Bromide (Br⁻) confirms</div>
Confirmatory test for I⁻ : 1. Perform Silver nitrate test as given above. 2. Layer Test: Perform Layer Test as given above.	<div>➤ Dark violet fumes are evolved which turns starch paper blue.</div> <div>Formation of yellow ppt. which is insoluble in ammonium hydroxide solution.</div> <div>Formation of violet layer.</div>	<div>Iodide (I⁻) Present</div> <div>Iodide (I⁻) confirms</div>
Confirmatory test for NO₃⁻ : Ring Test: Acidify soda extract with dil. Sulphuric acid and then add to it saturated solution of Ferrous Sulphate. Cool and add conc. Sulphuric acid carefully by the side of test tube without shaking.	<div>➤ Reddish brown coloured fumes becomes dense on heating with copper turnings.</div> <div>A deep brown ring at the junction of two liquids</div>	<div>Nitrate (NO₃⁻) Present</div> <div>Nitrate (NO₃⁻) confirms</div>

4. Detection of acidic radicals of Group III :

Test	Observation	Inference
Test for Sulphate (SO₄²⁻) : Acidify 2 ml soda extract with dil. Nitric acid and then add to it barium chloride or barium nitrate solution. Confirmatory test for (SO₄²⁻) : Acidify 2 ml soda extract with dil acetic acid and add to it lead acetate solution.	<div>Formation of white ppt which is insoluble in hot conc. Hydrochloric acid.</div> <div>Formation of white ppt which is soluble in ammonium acetate solution on heating</div>	<div>Sulphate (SO₄²⁻) present</div> <div>Sulphate (SO₄²⁻)confirms</div>

PART-II : DETECTION OF TWO BASIC RADICALS

ANALYSIS OF BASIC RADICALS

Separation of Basic radicals into Groups: On the basis of solubility product and reagents, the basic radicals are divided into the following five groups.

Group	Radicals	Group reagents
I	Pb^{2+} , Ag^+ , Hg_2^{2+}	Dil. HCl
II	Group-II A : (Copper group): Hg^{2+} , Cu^{2+} , Bi^{3+} , Pb^{2+} , Cu^{2+} , Cd^{2+} . Group-II B: (Arsenic group) : As^{3+} , Sb^{3+} , Sn^{2+} , Sn^{4+}	H_2S gas in the presence of dil. HCl
III A (Iron group)	Fe^{3+} , Al^{3+} , Cr^{3+}	NH_4Cl (Solid)+ NH_4OH solution
III B(Nickel group)	Ni^{2+} , Mn^{2+} , Zn^{2+} , Co^{2+}	H_2S gas in the presence of NH_4Cl (Solid)+ NH_4OH solution.
IV	Ca^{2+} , Sr^{2+} , Ba^{2+}	NH_4Cl (Solid)+ NH_4OH solution + ammonium carbonate (Solid).
V	Mg^{2+} , NH_4^+ , Na^+ , K^+	No specific reagent

Note: for the sake of convenience **Ammonium** (NH_4^+) is usually tested at the beginning of the analysis of the basic radicals. It is sometimes placed in a separate group known as **zero group**.

The systematic analysis of basic radicals involves following steps.

1. Preliminary test or dry test.
2. Detection of NH_4^+ (ammonium) radical.
3. Preparation of Original solution (O.S.)
4. Analysis of original solution by group reagent (Detection of group).
5. Analysis of the precipitate of a group.(Detection of basic radicals)

1. Preliminary test : State and Colour of the mixture also gives some information about the radicals present in the given mixture.

Colour of Mixture	Basic Radicals
Blue	Cu^{2+}
Blue-Green	Cu^{2+} , Fe^{3+} , Ni^{2+} , Cr^{3+}
Black to brown	Cu^{2+} , Mn^{2+} , Pb^{2+} , Co^{2+} , Ni^{2+} , Fe^{3+}
Pink-Brown	Mn^{2+} , Co^{2+}
Violet	Co^{2+}
Yellow	Sb^{3+} , As^{3+} , Ni^{2+} , Cd^{3+}
Red	Hg^{2+} , Pb^{2+}

2. Detection of NH_4^+ (Ammonium) radical.

Ammonium radical should be tested at the beginning as follows:

- (1) Take half spatula original mixture (solid) in a test tube, add 2 ml of dil. NaOH solution and heat. If smell of ammonia appears, presence of **ammonium** (NH_4^+) radical.
- (2) Hold a moist red litmus paper at the mouth of the test tube (Do not touch it to the test tube). The red litmus paper turns blue confirms **ammonium** (NH_4^+) radical.
- (3) Hold a glass rod dipped in conc. HCl near the mouth of the test tube . Formation of dense white fumes at the mouth of the test tube confirms **ammonium** (NH_4^+) radical.

3. Preparation of Original solution (O.S.)

For analysis of basic radical prepare original solution (O. S.) of the given mixture. Select the proper solvent in the order given below. Every time tae about 0.1 gm of the mixture in a clean test tube and try to dissolve in 2 ml of solvent.

- i) Distilled Water
- ii) Dil. Hydrochloric acid
- iii) Conc. Hydrochloric acid
- iv) Dil. Nitric acid
- v) Conc. Nitric acid
- vi) Aquaregia (3 parts of Conc. HCl + 1 part Conc. HNO₃)

If the mixture is not soluble in cold thn it is necessary to hat the contents. Allow such a hot solution to cool to room temperature before assuming that solvent is satisfactory. After the selection of solvent dissolve about 1 gm of the mixture in that solvent and proceed for the analysis of basic radicas. [Note: In case conc. HNO₃ or aquaregia is used, boil it off completely to dryness and dilute with distilled water].

The colour of the original solution (O.S.) may also indicate the presence of certain basic radicals.

Blue Solution -----	Cu ²⁺
Green solution-----	Cu ²⁺ , Cr ³⁺ , Fe ²⁺ , Ni ²⁺
Violet solution-----	Cr ³⁺
Reddish Brown or yellow-----	Fe ³⁺
Pink or Pink-brown -----	Co ²⁺ , Mn ²⁺

TABLE – 1

ANALYSIS OF FIRST GROUP BASIC RADICALS [Ag⁺ , Hg₂²⁺ Pb²⁺]

Warm the original solution in a test tube and then add dil. HCl drop with shaking. If white precipitate is formed indicates the presence of fist group. [Note: If original solution is prepared in dil. HCl or conc. HCl then first group is absent. Avoid excess HCl during precipitation]. Filter and wash the precipitate with cold water. Then boil the ppt. in water and filter while hot. Collect the filtrate

RESIDUE White : (Hg₂²⁺, Ag⁺) Wash with hot water 2 - 3 times and reject the washings. This removes lead, if any, present. Pour NH ₄ OH solution on the ppt. and collect the filtrate.		FILTRATE : (Pb²⁺) Divide into three parts. (A) Cool it under the tap white needle shaped crystals separate out (B) Add KI solution. A yellow ppt. Heat. The yellow ppt. dissolves. Cool. Golden yellow needle - shaped crystals appear (C) Add pot. chromate (K ₂ CrO ₄) solution. A yellow ppt. soluble in NaOH but insoluble in dilute acetic acid, is obtained. Lead (Pb²⁺) Present.	
RESIDUE Black ppt. : (Hg₂²⁺) Dissolve the residue in minimum quantity of aquaregia*. Evaporate to half its volume, dilute with water and divide into two parts. (A) Add one or two Cu foils and wait for 5 minutes. Cu foils turn silvery white. (B) Add stannous chlo-ride (SnCl ₂) solution in excess. A white ppt. turning grey. Mercurous (Hg₂²⁺) Present.	FILTRATE : (Ag⁺) Divide it into two parts. (A) Add dil. HNO ₃ in excess. A white ppt. (B) Add KI soln. A light yellow ppt. Silver (Ag⁺) Present		

ANALYSIS OF SECOND GROUP BASIC RADICALS

To the original solution add dil. HCl, warm and pass H₂S gas. Formation of coloured ppt. indicates the presence of second group. Filter and wash with water.

Colour of the ppt.	Basic radicals (is sulphids of metals)
Black ppt.	Hg ²⁺ , Pb ²⁺ , Cu ²⁺ , Bi ³⁺
Yellow ppt.	Cd ²⁺ , As ³⁺
Orange ppt.	Sb ³⁺
Brown ppt.	Sn ²⁺
Dirty yellow ppt.	Sn ⁴⁺

Separation of IIA (Copper group) and IIB (Arsenic group)

Wash the coloured ppt. with hot water. Then dissolve the ppt in dil. NaOH solution (or yellow ammonium sulphide). Boil and filter. [Note: If ppt. of II group is insoluble in dil NaOH then IIB is present and if it is soluble in dil. NaOH solution (or yellow ammonium sulphide) indicates IIA group].

RESIDUE: IIA GROUP
TABLE: 2

FILTRATE: IIB GROUP
TABLE: 3

TABLE - 2
ANALYSIS OF IIA GROUP RADICALS [Hg²⁺, Pb²⁺, Bi³⁺, Cu²⁺, Cd²⁺]

Boil the ppt. of IIA group with 50% of HNO₃ (equal part of conc. HNO₃ and water by volume) for few minute and filter. Collect the filtrate.

RESIDUE: Black ppt. (Hg²⁺) Dissolve in 2 ml of aquaregia and repeat the test as described under test of mercurous in Table - I. Mercuric (Hg²⁺) Present.	FILTRATE : [Pb²⁺, Bi³⁺, Cu²⁺, Cd²⁺] Take 2 ml of the filtrate in a test tube and add H ₂ SO ₄ . To this solution add few drops of methyl alcohol. If white ppt. is obtained indicates Pb ²⁺ then add dil. H ₂ SO ₄ to the whole filtrate. Add methyl alcohol to this solution and filter. Collect the filtrate.		
	RESIDUE: White ppt. Pb ₂ ⁺ Dissolve the white ppt.(residue) in ammonium acetate solution. To this add acetic acid and K ₂ CrO ₄ solution. Formation of yellow ppt. confirms Pb ²⁺ Lead (Pb²⁺) Present.	FILTRATE : [Bi³⁺, Cu²⁺, Cd²⁺] To the filtrate add NH ₄ OH (Excess). If white ppt. indicates Bi ³⁺ . Filter. Collect the filter.	
		RESIDUE: White ppt Bi³⁺ Dissolve it in minimum quantity of dilute HCl and divide into two parts. (A) Add sodium stannite soln. A black ppt. (B) Add it to a large excess of water. Water turns into milky. Bismuth (Bi³⁺) Present.	FILTRATE : Cu²⁺, Cd²⁺ (i) If the filtrate is colourless, Cu is absent. Now, pass H ₂ S. Yellow ppt. confirms Cadmium (Cd²⁺) (ii) If the filtrate is blue, both Cu ²⁺ and Cd ²⁺ may present. Divide this into parts. C.T. for Cu²⁺ : a) First part + dil. acetic acid drop by drop till decolourises. Now add pot. ferrocyanide K ₄ [Fe(CN) ₆] soln. A chocolate brown ppt. Copper (Cu²⁺) Present. C.T. for Cd²⁺ : b) To the second part add conc. HCl and pass H ₂ S gas. Filter and collect the filtrate. Dilute the filtrate with excess of water and pass H ₂ S gas. A yellow ppt. Cadmium (Cd²⁺) Present

TABLE - 3

ANALYSIS OF IIB GROUP RADICALS [Sb³⁺, As³⁺, Sn⁴⁺]

The filtrate for II B obtained after removal of II A is used for this purpose. To the filtrate add dil. HCl excess, ppt. obtained . Filter. Wash the residue with hot water. Boil the ppt. with conc. HCl and filter. Collect the filtrate.

RESIDUE Yellow ppt (As³⁺) : Wash the residue with water and divide into two parts. A. Heat the residue with water and powdered ammo-nium carbonate till it dissolves. Add dil. HCl. A yellow ppt. with or without passing H ₂ S. B. Boil the residue with conc. HNO ₃ until dissolved. Add ammonium molybdate soln. and heat. Wait a while. A yellow ppt. Arsenic (As³⁺) Present.	FILTRATE : (Sb³⁺, Sn⁴⁺) Add NH ₄ OH to make the filtrate just alkaline. Add 4 - 5 gms of solid oxalic acid. Boil and pass H ₂ S. Orange ppt. confirms Sb. Filter.	
	RESIDUE: Orange ppt (Sb³⁺) Dissolve the residue in conc. HCl. Boil off H ₂ S and divide into two parts. A. Add NH ₄ OH to neutralise the solution. Dilute with excess of water. White ppt. or turbidity. B. Add tin pieces and wait for sometime. A grey spongy deposit. Antimony (Sb³⁺) Present.	FILTRATE : (Sn⁴⁺) Boil off H ₂ S. Add zinc granules and dil. HCl. Keep it for sometime. Filter and divide the filtrate into two parts. A. Add ammonium molybdate soln. A deep blue ppt. or colour. B. Add mercuric chloride (HgCl ₂) soluton. A white ppt. turning grey. Tin (Sn⁴⁺) Present.

TABLE - 4

ANALYSIS OF III A GROUP RADICALS [Fe³⁺, Al³⁺, Cr³⁺]

Boil the original solution with few drops of conc. HNO₃ in order to convert Fe²⁺ into Fe³⁺. Cool. Add NH₄Cl_(Solid) and NH₄OH_(excess). Formation of coloured ppt. indicates the presence of IIIA group. Filter

Gelatinous white ppt. Al³⁺
Brown ppt. Fe³⁺
Dirty green ppt..... Cr³⁺

Dissolve the ppt. of IIIA group in minimum quantity of dil HCl. To this solution add 1 ml NaOH solution and 2 ml hydrogen peroxide solution. Boil for 2-3 minutes and filter. Collect the filtrate.

RESIDUE Brown ppt : (Fe³⁺, Cr³⁺) Dissolve the residue in NaOH solution and add excess of bromine water. Boil and filter.		FILTRATE : (Al³⁺). To the filtrate add solid NH ₄ Cl _(Solid) and boil. A white gelatinous ppt. Aluminium (Al³⁺) Present. .
RESIDUE Brown ppt : (Fe³⁺) Dissolve in dilute HCl and divide into two parts. A. First part + potassium ferrocyanide solution. Prussian blue ppt. or colour. B. second part + ammonium thiocyanate solution. Blood red colour. Iron (Fe³⁺) Present	FILTRATE : (Cr³⁺) Add excess of acetic acid and lead acetate solution. A yellow ppt. Chromium (Cr³⁺) Present.	

TABLE - 5

ANALYSIS OF III B GROUP RADICALS [Ni²⁺, Co²⁺, Zn²⁺, Mn²⁺]

To the original solution add NH₄Cl_(solid) and NH₄OH_(excess) . Warm and pass H₂S gas through the solution. Formation of ppt. indicates the presence of IIIB group. Filter. Colour of the ppt. indicates the presence of certain basic radicals.

- Black ppt. Ni²⁺, Co²⁺
- Grey ppt. Zn²⁺
- Pink ppt. Mn²⁺

Wash the ppt. with hot water. Dissolve the ppt. of III B in dil HCl. Boil and filter. Collect the filtrate

RESIDUE Black ppt : (Ni²⁺, Co²⁺) Dissolve the residue in aquaregia by heating if necessary. Evaporate the solution to remove excess of acid. Dilute the solution by adding nearly double its volume of water. [By adding water if blue colour changes to red, presence of cobalt is indicated]. Divide the solution into two parts.		FILTRATE : (Zn²⁺, Mn²⁺) Boil the filtrate and add NaOH solution in excess. Boil and filter. Collect the filtrate.	
First part: (Ni²⁺) Add excess of NH ₄ OH and then 2-3 drops of dimethyl- glyoxime (DMG) solution. A rose red ppt. Nickel (Ni²⁺) Present.	Second part : (Co²⁺) Again divide it into two parts. i) first part + Add NH ₄ Cl and NH ₄ OH in excess + potassium ferricyanide solution. warm. A reddish brown ppt. or colour obtained. ii) second part + little acetic acid and then potassium nitrite (KNO ₂). A yellow ppt. obtained Cobalt (Co²⁺) Present.	RESIDUE : (Mn²⁺) Dissolve the residue in dilute HNO ₃ . Add nearly 1gm of lead peroxide (PbO ₂) & 5 ml conc. HNO ₃ and allow the contents to settle. A purple colour in supernatant liquid. if necessary, dilute the supernatant liquid by adding water drop by drop. A purple colour. [Note : The colour is more pronounced on adding 2 - 3 drops of NH₄OH.] Manganase (Mn²⁺) Present	FILTRATE : (Zn²⁺) Divide the filtrate into two parts. i) First part + Pass H ₂ S gas. A white ppt. ii) Second part + dil. acetic acid and potassium ferrocyanide solution. A bluish white ppt. Zinc (Zn²⁺) Present.

TABLE - 6

ANALYSIS OF IV GROUP RADICALS [Ba²⁺, Sr²⁺, Ca²⁺]

To the original solution add NH₄Cl_(solid), NH₄OH_(excess) and (NH₄)₂CO₃ solution. Warm. Formation of white ppt. indicates the presence of IV group basic radicals. Filter and wash with hot water. Dissolve the ppt. in a minimum quantity of dilute acetic acid. To a small portion of this solution add potassium chromate (K₂CrO₄) solution. If yellow ppt. is obtained, barium is present. If so, then add potassium chromate (K₂CrO₄) solution to whole solution. Shake and filter. Collect the filtrate. [Note; If no yellow ppt. with potassium chromate (K₂CrO₄) solution then test for Sr²⁺ and Ca²⁺, from the remaining portion of the solution].

RESIDUE Yellow : (Ba²⁺) The yellow precipitate itself confirms presence of barium. Barium (Ba²⁺) Present.	FILTRATE : (Sr²⁺, Ca²⁺) To the filtrate (or remaining portion of the solution, if Ba ²⁺ is absent) add ammonium acetate solution in excess. Warm and scratch the sides of the test tube with a glass rod and wait a little. A white ppt. is obtained. Filter. Collect the filtrate.	
	RESIDUE White : (Sr²⁺) The white precipitate itself confirms presence of strontium. Strontium (Sr²⁺) Present	FILTRATE : Ca²⁺) To the filtrate add ammonium oxalate solution. Formation of white ppt. confirms the presence of calcium. Filter. Dissolve the white ppt. in dil. H ₂ SO ₄ and add few drops of dil. KMnO ₄ soln. warm. Pink colour of KMnO ₄ solution is discharged. Calcium (Ca²⁺) Present.

ANALYSIS OF V GROUP RADICALS [Mg²⁺, NH₄⁺]

Like other groups, there is no common reagent which can precipitate all the radicals of V group. Hence, the radicals are tested individually.

1. **Magnesium (Mg²⁺)** : To the original solution add NH₄Cl_(solid), NH₄OH_(excess) and then Na₂HPO₄ (disodium hydrogen phosphate) solution. Shake well and scratch the sides of test tube with glass rod.
Formation of a white crystalline precipitate confirms **magnesium (Mg²⁺)** radical.
2. **Ammonium (NH₄⁺)** : Please see the test of ammonium(NH₄⁺) on page no. 2

Result :

The given inorganic mixture was found to contain

Acidic radicals : _____ () and _____ ()

Basic radicals : _____ () and _____ ()
